

## Supplementary Information

### Oxido- and dioxido-vanadium(V) complexes supported on carbon materials: reusable catalysts for the oxidation of cyclohexane

Manas Sutradhar<sup>1,\*</sup>, Marta A. Andrade<sup>1</sup>, Sónia A. C. Carabineiro<sup>1,2,3,\*</sup>, Luísa M. D. R. S. Martins<sup>1,\*</sup>, M. Fátima C. Guedes da Silva<sup>1</sup> and Armando J. L. Pombeiro<sup>1,4</sup>

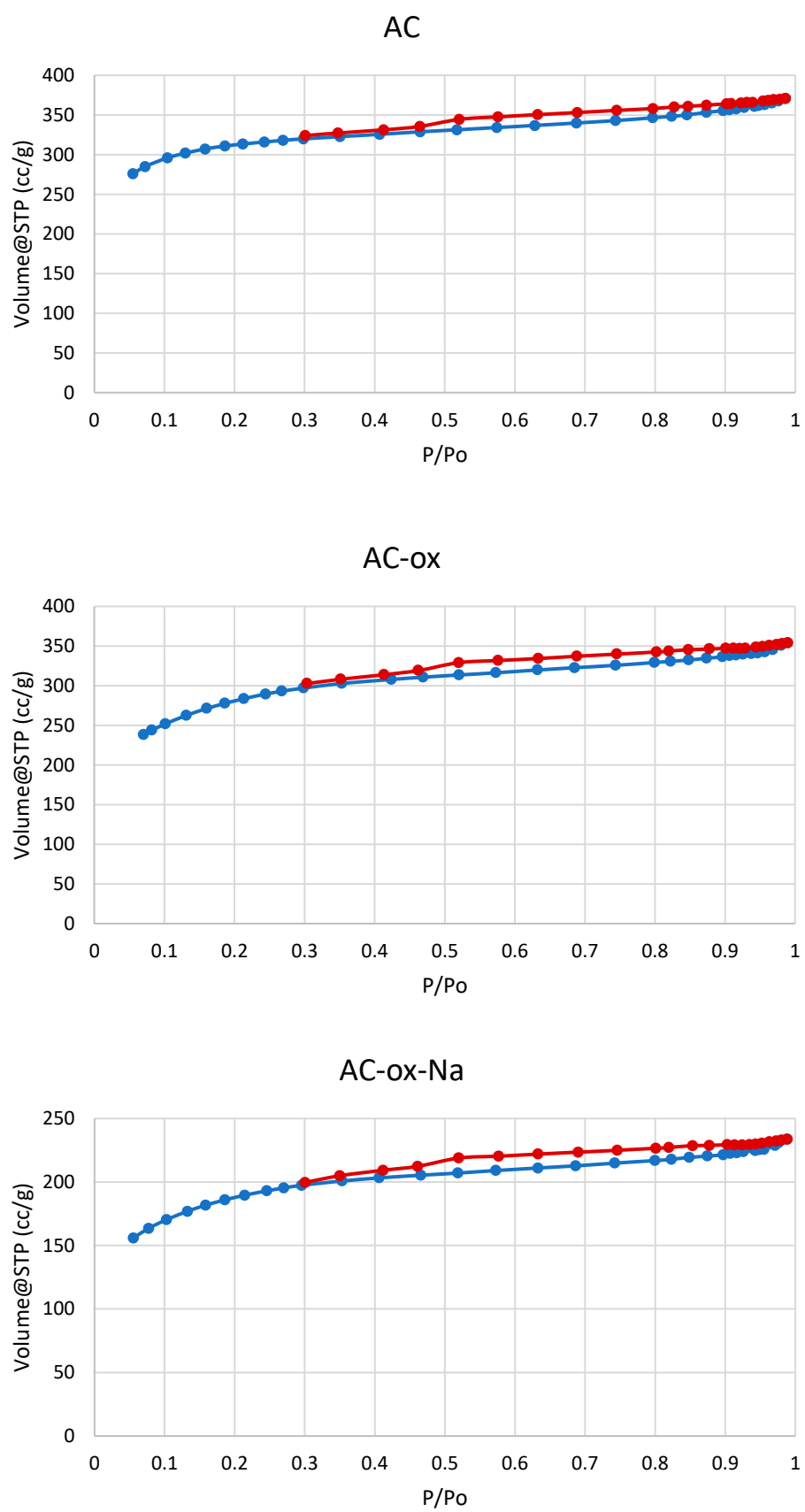
<sup>1</sup> Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal.

<sup>2</sup> Laboratory of Catalysis and Materials (LCM), Associate Laboratory LSRE-LCM, Faculty of Engineering, University of Porto, 4200-465 Porto, Portugal

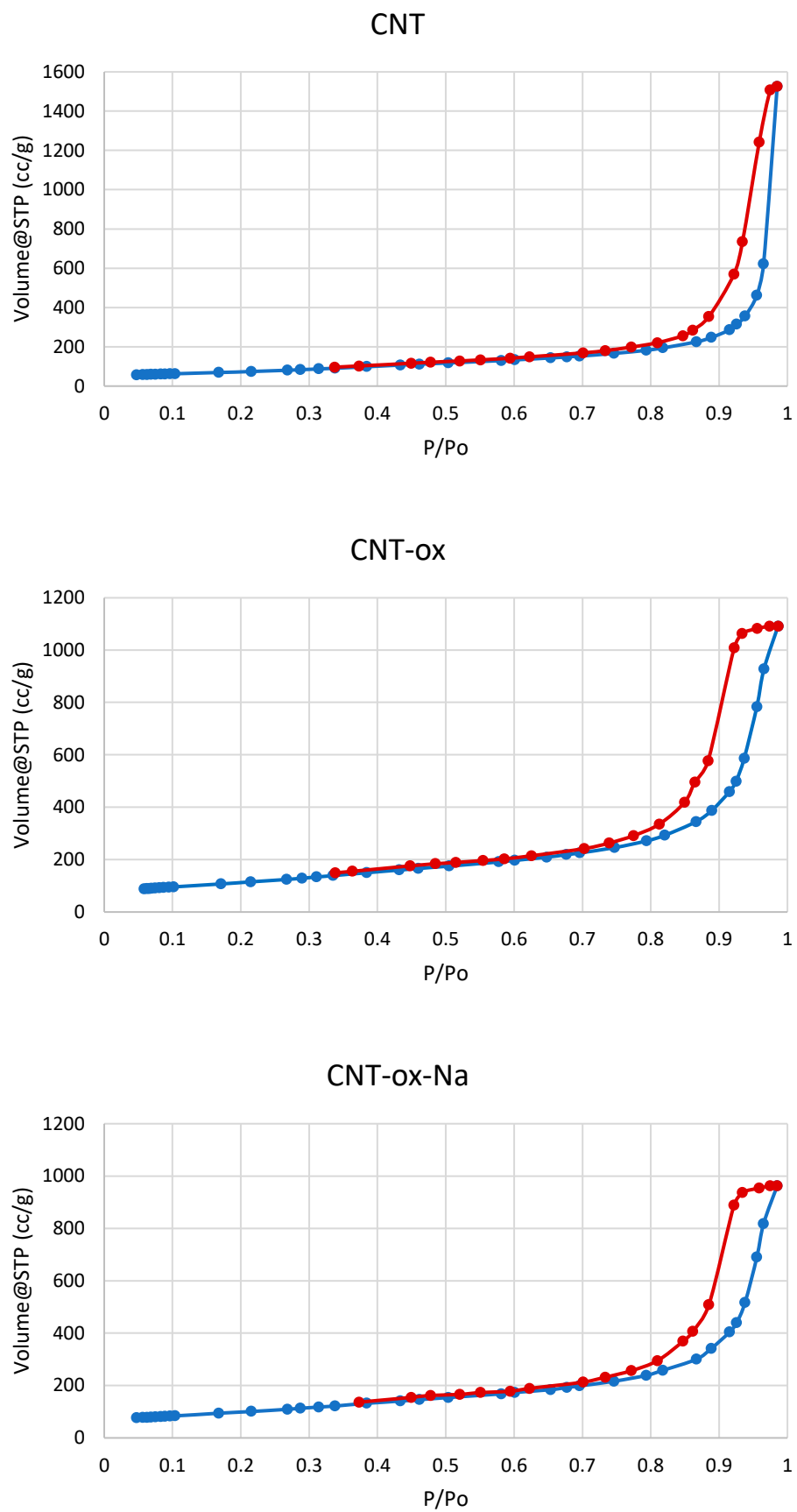
<sup>3</sup> LAQV-REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade NOVA de Lisboa, Largo da Torre, 2829-516 Caparica, Portugal.

<sup>4</sup> Peoples' Friendship University of Russia (RUDN University), Research Institute of Chemistry, 6 Miklukho-Maklaya Street, Moscow 117198, Russian Federation

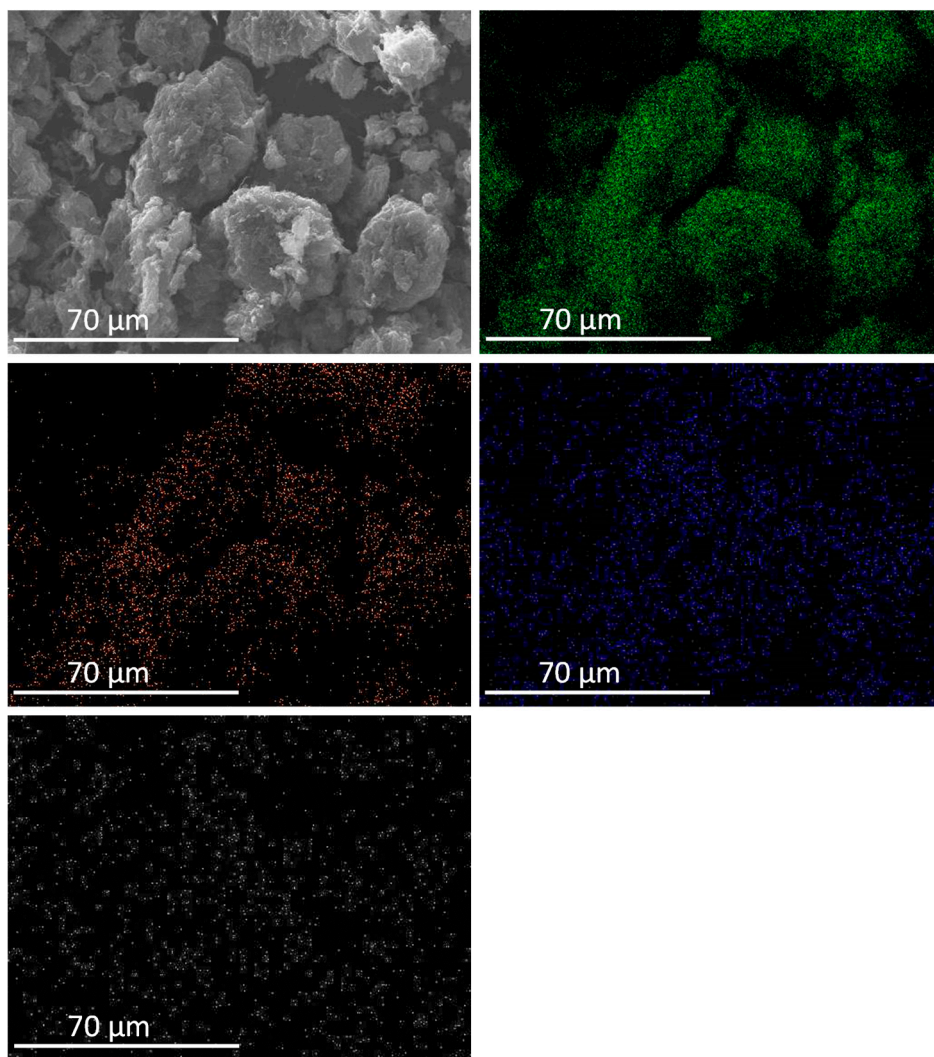
\* Correspondence: manas@tecnico.ulisboa.pt (M.S.), sonia.carabineiro@fct.unl.pt (S.A.C.C.), luisammartins@tecnico.ulisboa.pt (L.M.D.R.S.)



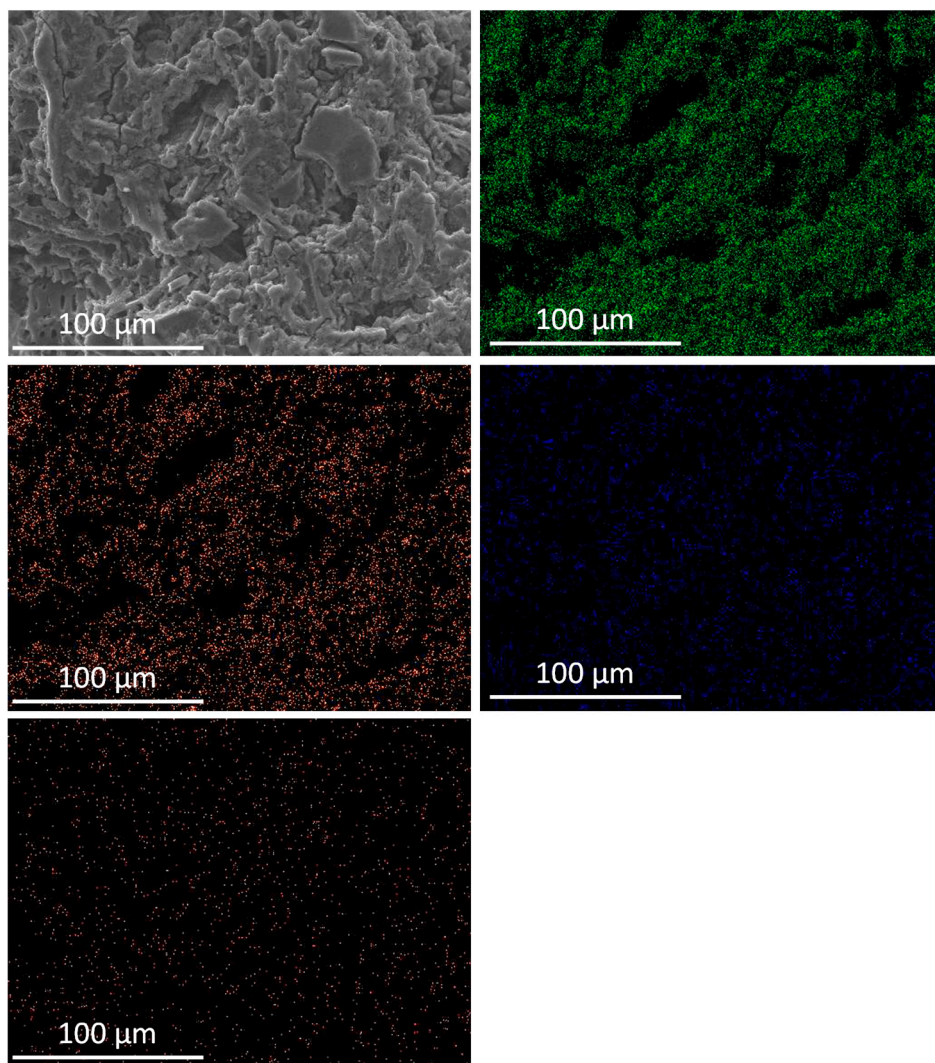
**Figure S1.** N<sub>2</sub> adsorption isotherms of AC, AC-ox, AC-ox-Na.



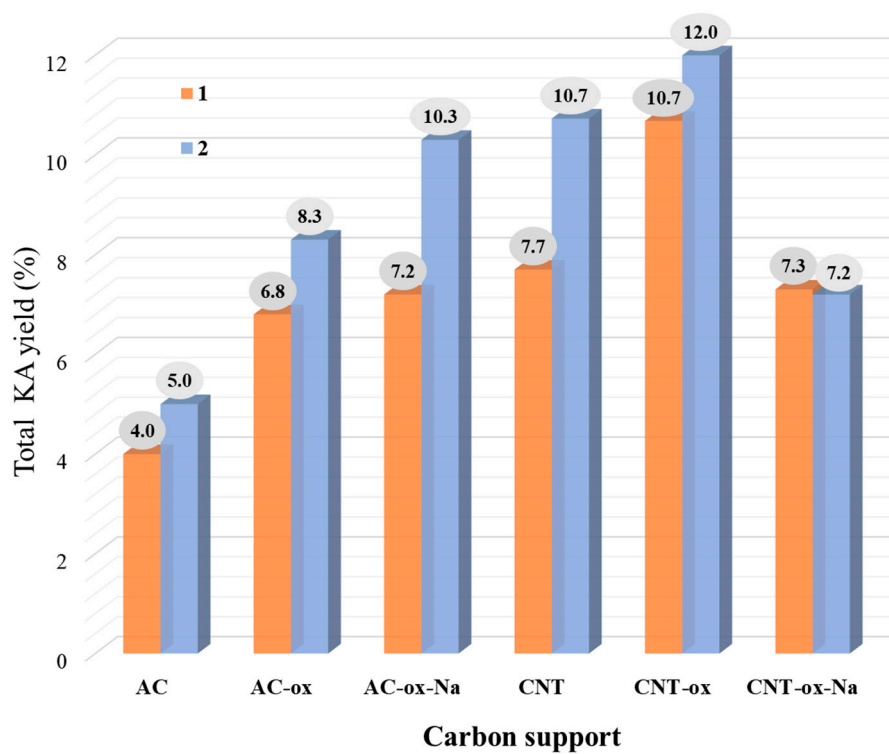
**Figure S2.** N<sub>2</sub> adsorption isotherms of CNT, CNT-ox, CNT-ox-Na.



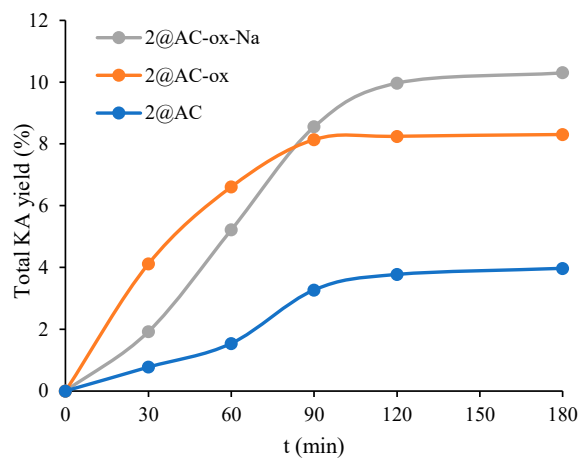
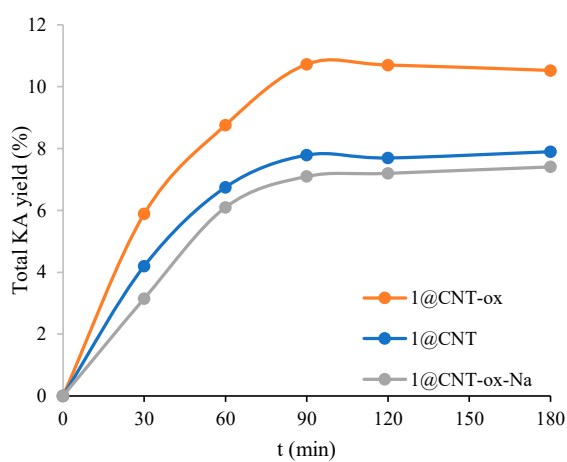
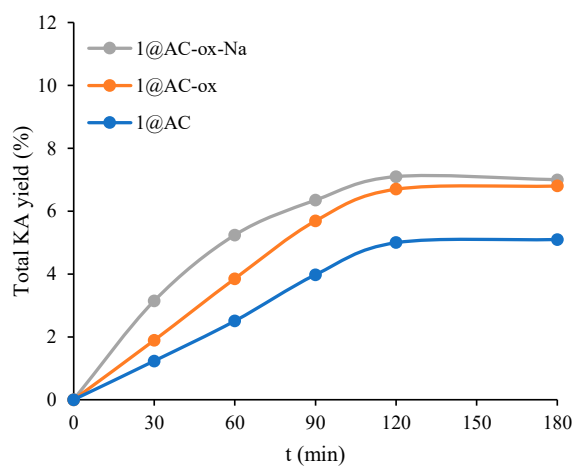
**Figure S3.** SEM-EDX mapping for sample V1@CNT-ox: C (green), O (pink), Br (blue) and V (white).



**Figure S4.** EDX mapping for sample **V2@AC-ox**: C (green), O (pink), Br (blue) and V (white).



**Figure S5.** Total yield of KA oil obtained by the MW-assisted oxidation of cyclohexane at 80 °C, 20 W, for 2 h, supported on different carbon materials.



**Figure S6.** Effect of the duration of the MW irradiation on the catalytic activity of supported oxidovanadium complexes for the oxidation of cyclohexane with TBHP in MeCN.

**Table S1.** Summary of uses of carbon-supported oxidovanadium complexes in various catalytic reactions and major outcomes.

Reaction	Vanadium complexes	Carbon support	Catalytic results	Catalyst stability	Ref
1-phenylethanol oxidation	Oxovanadium (V)	Functionalized MWCNT, AC and CX	96 % acetophenone yield, > 98% selectivity	90 % of the catalytic activity was observed by the 10th cycle.	[1]
Oxidation of alcohols	Oxovanadium Schiff base	Graphene nanosheets	96 % of benzohydrazone	Efficient recycling of the catalyst over six runs.	[2]
Cyclooctene oxidation	Hydroxyl functionalized oxovanadium(IV) Schiff-base	Modified MWCNT	Cyclooctene epoxide (08.6%), cyclooctene-1-ol (52.5%) and cyclooctene-1-one (28.9%).	Reused for three times without neither loss of activity or selectivity.	[3]
Styrene oxidation	Oxovanadium(IV) acetylacetonate	Amino-modified CMK-3	66.7 % yield of styrene oxide with a selectivity of 70.5 %	A decrease of 10 % in conversion and < 10 % selectivity to styrene oxide were reported.	[4]
Styrene epoxidation	Oxovanadium(IV) salen	Amino-modified graphene oxide	18.5 % styrene epoxide, and 21% selectivity	Three recycling runs for the catalyst with a 10 % conversion drop and slight selectivity decrease (< 5%).	[5]
	Oxovanadium(IV) salen	Carbon-coated Fe <sub>3</sub> O <sub>4</sub> hybridized with graphene	54.6 % yield of styrene epoxide with 59.2% selectivity	For two cycles, almost no leaching was observed; both yields and selectivity were maintained.	[6]
	Oxovanadium(II) Schiff base	Amino-functionalized graphene oxide	16.7 % yield of styrene epoxide with 20.7 % selectivity	No significant loss of activity and selectivity after successive runs (<5 %).	[7]
Epoxidation of oleic acid	Oxovanadium Schiff base	Functionalized graphene oxide	98.9 yield of the epoxide with 99.1 % selectivity	The catalysts could be successfully recycled and reused for six runs without a significant decrease in activity or selectivity.	[8]
Epoxidation of geraniol	Oxovanadium(IV) acetylacetonate	CMK-3	Conversions > 98% and 98-99% selectivity for 2,3-epoxygeraniol	For two cycles, almost no leaching was observed; both yields and selectivity were maintained.	[9]
Oxidation of p-chlorobenzenethiol	Oxovanadium (IV) complex	Amino functional microporous organic nanotube frameworks	100 % conversion was reported with 98 % selectivity.	The material was recycled more than 8 times with no apparent decrease in catalytic activity	[10]



**Table S2.** Supported vanadium complexes in cyclohexane oxidation and major outcomes.

Vanadium complexes	Support	Yield (%)			Selectivity to KA oil (%)	Catalyst stability	Ref
		A	K	O			
Oxidovanadium(V)	Functionalized AC and CNT	7.0	5.0	-	~100	Activity drop of 28 % by the 4 <sup>th</sup> cycle.	This work
Functionalised oxidovanadium(IV) Schiff-base	Modified MWCNTs	62.5	8.9	7.5	90.5	No leaching was observed.	[11]
Oxidovanadium(IV)	PDMS	4.7	1.0	-	~100	The activity of the recycled catalyst was much lower.	[12]
V-scorpionate complex	MOR zeolite	7.9	43.9	-	~100	Loss of activity in the recycling tests: 18 % in the 4 <sup>th</sup> cycle.	[13]
Vanadium phosphate	Mesoporous KIT-6 silica	4.9	8.6	5.8	69.9	A conversion decrease of 30 % was observed by the 5 <sup>th</sup> cycle.	[14]
VO <sub>2</sub>	HTS (TiO <sub>2</sub> -modified material)	0.1	2.7	13.4	21.7	-	[15]
Vanadium phosphorus oxide (VPO)	SBA-15 and TUD-1 silicas	1.0	30.0	-	~100	-	[16]

A- cyclohexanol; K- cyclohexanone; O- others; AC-activated carbon; CNT- carbon nanotubes.

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